

상분리된 블록공중합체 미세구조의 나노공학에의 응용: 나노패터닝과 나노입자 제조

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Phase Separated Block Copolymers Microdomains for Nanotechnology: Nanopatterning and Nanoparticle FabricationCheolmin ParkDepartment of Metallurgical System Engineering, School of engineering
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Creating a regular surface pattern on the nanometer scale is important for many technological applications, such as the periodic arrays constructed by optical microlithography that are used as separation media in electrophoresis, and island structures used for high-density magnetic recording devices.[1,2] Block copolymer patterns can also be used for lithography on length scales below 50 nanometers thanks to not only the scale of microdomains but also convenience to tune the size of microdomains with changing their molecular weights.[3]

For such copolymers to prove useful for thin-film technologies, however, chemically patterned surfaces need to be made substantially defect-free over large areas, and with tailored domain orientation and periodicity. Control over domain orientation has been achieved by several routes, using electric fields, temperature gradients, patterned substrates and neutral confining surfaces.[4]

Micropatterned block copolymer structures have also been used to sequester small organic and inorganic particles, including metallic ones, into selected microdomains.[5] In addition, block copolymer microdomains have been used as nanoscale reactors in which small-scale particles are templated and grown.[6] And recently, electroless deposition of metals into selective microdomains has been performed to provide continuous material loading.[7]

Here we address two ways to utilize block copolymer microdomains in both cases: control of block copolymer microdomains and fabrication of nano-particles via a block copolymer template. First of all, we describe an extremely fast process that leads the formation of two-dimensional periodic thin films having large area and uniform thickness. The process includes a new type of interaction (directional crystallization of a solvent) with block copolymer microdomains. This new method is based on the use of crystalline organic materials, which are solvents for the block copolymers above their melting temperatures. The directional crystallization of the solvent leads to the directional microphase separation of the block copolymer. Combined with a topographically pre-patterned substrate, the process allows further control of the block copolymer patterns. Subsequent removal of selective microdomains by oxygen plasma reactive ion etching generates regularly patterned holes, which may be useful for nanolithographic template.

In the second approach, we introduce a new block copolymer having iron molecules. The block copolymer releases and subsequently converts its mobile iron molecules into iron oxide nanoparticles with thermal treatment under oxygen environment. The phase separated microdomain structure helps control the size distribution of the nanoparticles created on the block copolymer surface.

Experimental

We employed a polystyrene PS-*block*-polyisoprene diblock copolymer, denoted PS/PI(45/12), having a PS block of 45,000 g/mol and a PI block of 12,000 g/mol. The bulk microdomain structure, determined by Small Angle X-ray Scattering (SAXS), is that of hexagonally packed, cylindrical PI domains with an intercylinder distance (d_0) of 48 nm and cylinder diameters of 20 nm. The patterned substrate was produced by standard lithographic techniques at the MIT Microsystems Technology

Laboratories. The substrate pattern consists of 30 nm high, $2 \mu\text{m}^2$ mesas arranged in a square array with a $4 \mu\text{m}$ spacing as shown in the schematic diagram of Figure 2a.

The directional solidification method described in detail in our previous work[8] was performed using either a glass substrate or a pre-patterned substrate. A block copolymer film was cast from xylene solution $\sim 0.3 \text{ wt}\%$ onto a glass coverslip. This film was covered by benzoic acid (BA) powder, confined by the patterned substrate or another slide, and heated to $150 \text{ }^\circ\text{C}$, leading to a clear homogeneous solution. The solution was then supercooled by placing the substrate on a hot temperature gradient $10 \text{ }^\circ\text{C}/\text{cm}$ bar at $110 \text{ }^\circ\text{C}$ to induce directional crystallization of the BA, resulting in large, elongated crystals with the b axis parallel to the growth front direction. The sample was moved to a position on the hot bar corresponding to a temperature of $60 \text{ }^\circ\text{C}$ and held for 1 min to complete the crystallization of the BA, then cooled to room temperature. In using the pre-patterned substrate, the topography of the substrate gives rise to thickness variations in the directionally solidified block copolymer thin films. Thickness variations result from the copolymer confinement between the flat BA single crystal and the topographically patterned substrate. The samples prepared by the process were stained with OsO_4 for 4 hrs for transmission electron microscope (TEM).

For fabrication of nano scale particles on a substrate, iron-centered polyoxazoline block copolymers, $[\text{Fe}\{\text{bpy}-(\text{PEOX-PUOX})_2\}_3]^{2+}$ were prepared. The details of the polymer synthesis and characterization is found in our previous literature.[9] Thin films ($\sim 30\text{-nm}$ thick) were cast on carbon-coated 200-mesh TEM copper grids from $0.1 \text{ wt}\%$ chloroform solution. Thin films were annealed for 2 days under vacuum at 160°C in an oven. The samples were exposed to RuO_4 vapor for 1 hr to stain PEOX domains selectively.

Samples were examined with a JEOL 200 CX TEM operated at 200 kV in bright field mode and with tapping mode atomic force microscope (AFM), (Nanoscope III) in amplitude contrast mode.

Results and Discussion

I. Control of block copolymer microdomains

A bright-field TEM image of a thin film of the PS/PI (45/12) block copolymer with the thickness of approximately 50 nm, directionally solidified with BA, on a normal glass slide is shown in Figure 1a. The darker regions in Figure 1a correspond to the OsO_4 -stained PI microdomains. It is apparent that the PI cylinders, lying in-plane, are well oriented along the crystallographic b axis of the BA (the fast crystal growth direction). The ordered parallel cylinder structure also extends over regions larger than $50 \mu\text{m}^2$. Fast Fourier Transformed (FFT) spectrum in the inset of the Figure 1a shows multi-order reflections, confirming large area orientation. The average diameter of the PI cylindrical microdomains is approximately 20 nm, while the average distance between the cylinders is 40- 50 nm consistent with the bulk SAXS data. In-plane PI cylinders are aligned along the BA b axis. We assume the lower surface tension PI block is preferentially at the carbon interface while the PS block forms the interface with the BA surface due to its more favorable interaction.

An interesting possibility to achieve vertically aligned cylinders is to employ ultrathin films of a cylinder forming block copolymer.[10] An initially thinner PS/ PI film (approximately 20 nm thickness) prepared from a more dilute solution probably first forms a thin metastable vertically oriented lamellar film which undergoes a vertical undulation instability, resulting in a vertically aligned cylindrical structure. Figure 1b shows a bright-field TEM image of PS/PI (45/12) block copolymer directionally solidified with BA and stained with OsO_4 . The dark OsO_4 -stained vertically aligned cylindrical PI microdomains are oriented into rows along the b axis of BA crystal. The aligned vertical cylinders again extend over regions larger than $50 \mu\text{m}^2$. The FFT power spectrum in the inset of Figure 2b shows spot like first reflections with 6-fold symmetry, indicating approximate hexagonal packing of the PI microdomains.

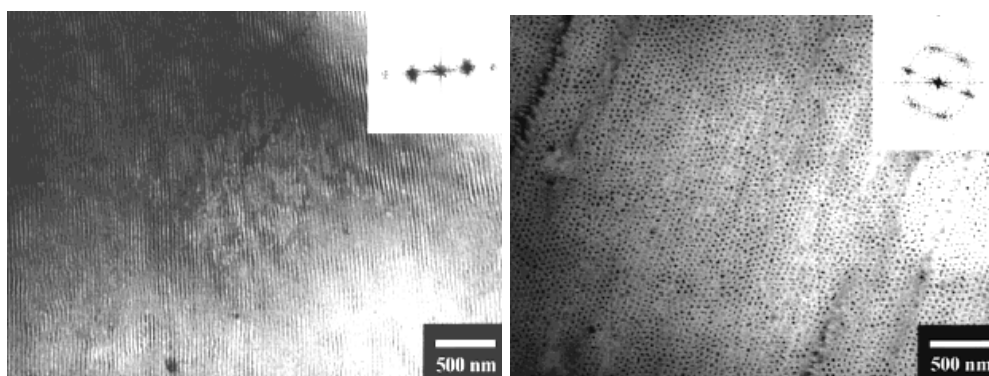


Figure 1. Bright field TEM micrographs of PS/PI (45/12) block copolymer films directionally solidified via crystallization of BA with the thickness of approximate 50 nm (a) and 20 nm (b) respectively

In order to further control the block copolymer microdomain orientation, we introduced a topographically pre-patterned substrate. The block copolymer film between BA crystal and the pre-patterned substrate induced thickness variation of the films, which are thinner on the mesas and thicker in the plateau regions. A AFM image after O₂-RIE is shown in Fig. 2b. This image, taken in amplitude contrast mode, reveals the double orientation of the cylindrical PI microdomains. After O₂-RIE, the center-to-center spacing of both vertically aligned and in-plane cylinders is approximately 48 nm, comparable to that in the bulk. In the thicker film regions, cylindrical PI microdomains are well aligned along the *b* axis of the BA crystal with the cylinder axis parallel to the substrate and to the walls of the mesas. In the thinner film regions, the PI cylinders are hexagonally packed with their cylinder axes perpendicular to the substrate.

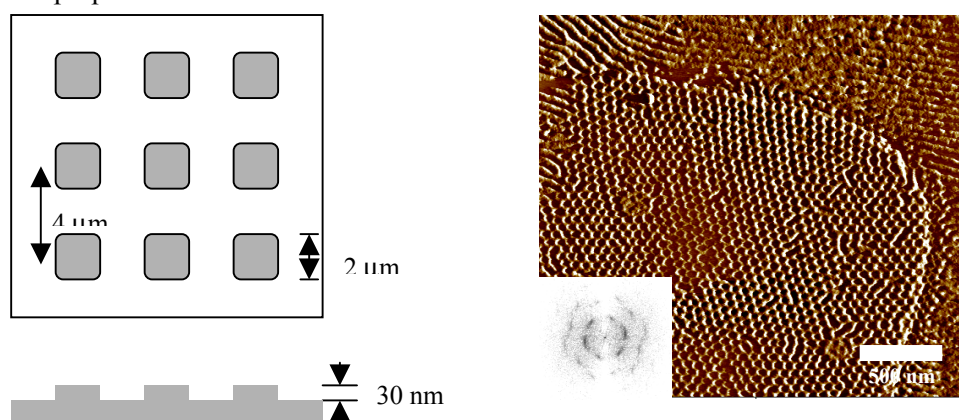


Figure 2. (a) Schematics of the topographically pre-patterned substrate. (b) AFM image of PS/PI (45/12) block copolymer film directionally oriented on the pre-patterned substrate via crystallization of BA.

II Fabrication of iron-oxide nano-particles

Bright-field TEM micrographs of the thin films (30nm) of the [Fe{bpy(PEOX-PUOX)₂}₃]²⁺ block copolymer annealed at 160 °C for 2 hrs are shown in Figure 3. A bright-field TEM micrograph of the stained sample, shown in Figure 3a, clearly displays both the microdomain structure and randomly distributed nanoscale clusters with sizes ranging from 20 to 40 nm. Staining for 1 h with RuO₄ provided good contrast. Due to different diffusivities of staining agent in the amorphous PEOX and crystalline PUOX microdomains and/or to the chemical affinity of RuO₄ for the amide group in the PEOX blocks, we speculate that the dark circular areas correspond to the PEOX microdomains. These dark convex-shaped microdomains are ~15 nm in diameter and spaced about 27 nm apart.

Nanoscale clusters generally appear randomly distributed; however, local preference to PEOX microdomains is observed as shown in Figure 3a. A bright-field TEM micrograph of the unstained, annealed sample, shown in Figure 3b, visualizes only the nanoscale clusters. Amplitude contrast makes iron clusters with higher electron density appear dark. The clusters in thin films likely arise from kinetically unstable bonding of the metal to the macroligand. Thus, when the block copolymer is annealed, the iron ions become mobile, aggregate, and oxidize, ultimately forming clusters of varying sizes. Because the affinity of Fe (in low oxidation states) for oxygen is very high, we can speculate that heating the sample when exposed to air allows oxidation to occur, leading to iron oxides such as Fe_2O_3 and FeO .

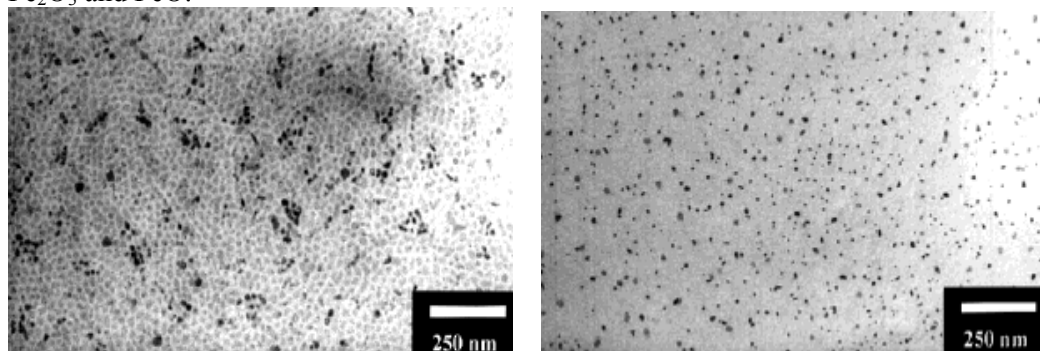


Figure 3. Bright-field TEM plan view images of the thin films of the $[\text{Fe}\{\text{bpy}\{\text{PEOX-PUOX}\}_2\}_3]^{2+}$ block copolymer. (a) Stained, annealed sample displays both small clusters with the size of $\sim 20\text{-}40$ nm and a cylindrical PEOX microdomain structure. (B) Unstained, annealed sample only shows a small cluster structure.

Conclusions

We presented two different approaches for potential nanoscientific applications, using block copolymers. One is to use block copolymers for creating nano-scale regular patterns. The other is to generate nano-scale inorganic particles by the help of phase separated block copolymer microdomains. The former is achieved by a process including a new type of interaction (directional crystallization of a solvent) with block copolymer microdomains to produce a long range order. The combination of a topographically pre-patterned substrate with the process allows further control of the block copolymer patterns. Subsequent removal of selective microdomains by oxygen plasma reactive ion etching generates regularly patterned holes, which may be useful for nanolithographic template.

In the second way, a block copolymer is used as a template to create nanoscale oxide particles on its surface. A designed block copolymer containing iron molecules converts its iron molecules into iron oxide nanoparticles with thermal treatment under oxygen environment. The phase separated microdomain structure helps control the size of the nanoparticles created on the polymer surface.

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